

Phosphorus and dissolved silicon dynamics in the River Swale catchment, UK: a mass-balance approach

M. J. Bowes and W. A. House*

Centre for Ecology and Hydrology, Winfrith Technology Centre, Winfrith Newburgh, Dorchester, Dorset DT2 8ZD, UK

Abstract:

The internal riverine processes acting upon phosphorus and dissolved silicon were investigated along a 55 km stretch of the River Swale during four monitoring campaigns. Samples of river water were taken at 3 h intervals at sites on the main river and the three major tributaries. Samples were analysed for soluble reactive phosphorus, total dissolved phosphorus, total phosphorus, dissolved silicon and suspended solid concentration. Mass-balances for each determinand were calculated by comparing the total load entering the river with the total load measured at the downstream site. The difference, i.e. the residual load, showed that there was a large retention of phosphorus and silicon within the system during the March 1998 flood event, but the other three campaigns produced net-exports.

Cumulative residual loads were calculated for each determinand at 6 h intervals throughout each campaign. This incremental approach showed that the mass-balance residuals followed relatively consistent patterns under various river discharges. During stable low-flow, there was a retention of particulate phosphorus within the system and also a retention of total dissolved phosphorus and soluble reactive phosphorus, most likely caused by the sorption of soluble phosphorus by bed-sediments. In times of high river-discharge, there was a mobilization and export of stored bed-sediment phosphorus. During overbank flooding, there was a large retention (58% of total input) of particulate phosphorus within the system, due to the mass deposition of phosphorus-rich sediment onto the floodplain. Soluble phosphorus was also retained within the system by sequestration from the water column by the high concentration of suspended solids.

The dissolved silicon mass-balance residuals had a less consistent pattern in relation to river discharge. There was a large retention of dissolved silicon during overbank flooding, possibly due to sorption onto floodplain soil, and net-exports during periods of both stable low-flow and rising limbs of hydrographs, due to release of dissolved silicon from pore-waters. Copyright © 2001 John Wiley & Sons, Ltd.

KEY WORDS phosphorus; silicon; River Swale; mass-balance; suspended sediment; bed-sediment; nutrient transport

INTRODUCTION

The movement, retention and transformation of phosphorus and dissolved silicon in river systems is of great environmental interest, as the elements are potentially limiting nutrients in most freshwater environments. The internal processes acting upon phosphorus within rivers are complex, involving interactions with interstitial pore-waters, suspended sediments, bed-sediments, benthic algae, macrophytes, and also chemical precipitation and dissolution reactions (Jordan-Meille *et al.*, 1998). Owing to this complexity, previous studies have tended to investigate these relationships on a small scale, either in the laboratory (House *et al.*, 1995; House and Denison, 1998; House and Warwick, 1999) or by studying very small stretches of rural streams (Meyer and Likens, 1979; Hill, 1981; Dorioz *et al.*, 1989; Jordan-Meille *et al.*, 1998). Dissolved reactive silicon is also an important nutrient for diatom growth and has been implicated as a limiting nutrient in some large river systems (Admiraal *et al.*, 1993). Dissolved silicon may be released from bed-sediment pore-waters, assimilated in benthic diatom biofilms and also undergo reactions in soil solutions (Reynolds, 1986; Brown and Mahler, 1988; Zhmud *et al.*, 1997).

*Correspondence to: Dr. W. A. House, CEH Dorset, Winfrith Technology Centre, Winfrith Newburgh, Dorchester, DT2 8ZD, Dorset.

Received 6 December 1999

Accepted 22 May 2000

Many catchment-scale studies have used mass-balances (a comparison of the inputs into a river system with the exports from the catchment) as a way of observing phosphorus dynamics. This requires the direct measurement or reliable estimation of all major phosphorus (P) inputs and outputs from the catchment at short time intervals (typically less than 12 h) over long periods of time. Because of the operational difficulties in such intensive fieldwork, previous studies have used less frequent sampling and mathematical modelling to determine seasonal patterns of phosphorus processing and export, or general trends related to river discharge (Aiba and Ohtake, 1977; Jaworski *et al.*, 1992; Brunet and Astin, 1998; Hetling *et al.*, 1999).

The mass-balance approach has been used previously to study the in-stream processing of phosphorus within the River Swale catchment, as part of the Land–Ocean Interaction Study (LOIS) (House and Warwick, 1998a,b). These studies have attempted to measure all tributary phosphorus inputs to the river at 2 h intervals during three 100 h intensive sampling campaigns and have shown that there was a net retention of phosphorus within the river system over the duration of the sampling campaigns. The fact that net losses were not observed is probably because of the episodic nature of phosphorus export from the river system, as highlighted in previous work (Jordan-Meille *et al.*, 1998). Therefore, the duration of the monitoring campaigns in this study was extended to approximately 200 h to cover more varied changes in river discharge than hitherto possible and also to increase the chance of periods of phosphorus export being observed. This study aims to use a new mass-balance approach to study subtle changes in soluble and particulate phosphorus, as well as dissolved silicon movement within the River Swale catchment, over a range of flow conditions throughout a year.

Study area

The River Swale catchment covers an area of 1457 km². It drains the eastern side of the Pennine hills, Northern England, before flowing in a south-easterly direction to the confluence with the River Ure (Figure 1). The upper part of the catchment consists of small, acidic, upland streams flowing within narrow, steep-sided valleys. The water is soft at the source, but becomes progressively harder as it flows eastwards over carboniferous limestone. This upland area is dominated by moorland and low intensity agriculture, mainly sheep farming.

This study concentrates on a 55 km lowland stretch of the river, between Catterick Bridge (in the piedmont zone) and Crakehill (10 km upstream of the confluence with the River Ure). The underlying bedrock of the

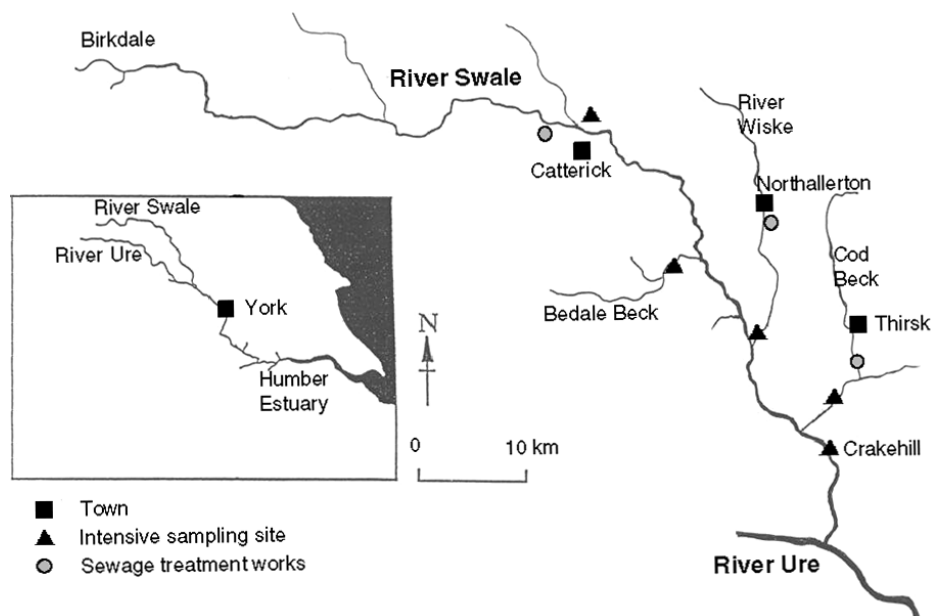


Figure 1. River Swale catchment, indicating the position of the intensive sampling sites and sewage treatment works

studied section is triassic new red sandstone. The substrate in the uppermost part of the reach consists of coarse gravels and boulders (Taylor and Macklin, 1997), resulting in a wide, braided channel. In the middle and lower stretches of the study reach, the river becomes much deeper, and is confined to its channel by large, man-made flood defence levees along almost the entire length of the river. The width of the river at the water surface varied between 11 and 44 m, with an average of *c.* 20 m (House and Warwick, 1999), which gives the study reach an estimated bed area of $1.1 \times 10^6 \text{ m}^2$.

The floodplain within this reach consists of high quality agricultural land, which is mainly used for arable, sheep, cattle, pig and poultry farming. A more detailed description of the geology, geomorphology and land-use of the River Swale catchment can be found in Jarvie *et al.* (1997) and Taylor and Macklin (1997).

The study reach contains the three urban areas of Catterick, Northallerton and Thirsk, which contribute phosphorus to the River Swale *via* sewage treatment works (STWs). The STW effluent from Catterick is discharged directly into the River Swale at Colburn (3 km upstream of Catterick Bridge). Colburn and the upper Swale STWs have a population equivalent (PE) of 25 800. The Northallerton STW discharges into the River Wiske (PE of 25 500) and Cod Beck receives the STW effluent from Thirsk (PE of 17 500). Bedale Beck also receives STW effluent (PE of 13 000).

METHODS

Intensive sampling campaigns

Four intensive sampling campaigns were undertaken on the catchment between March 1998 and February 1999. The date and duration of these campaigns are shown in Table I. Water samples were taken at three hourly intervals from the main river sites at Catterick Bridge and Crakehill (Figure 1) and from its three major tributaries of Cod Beck, River Wiske and Bedale Beck (Table I). All five sampling points were located at Environment Agency gauging stations. The 500 ml water samples were taken using automatic water samplers (EPIC, model 1011), with inlet pipes positioned at a fixed height above the bed of the river (approximately at the midpoint of the water column at the time of installation).

In addition, the majority of the 15 minor tributaries between Catterick and Crakehill were sampled once per campaign. Their discharges were determined by measuring their cross-sectional area and the flow velocity at 60% of the total depth, using an ultrasonic flow meter (SENSA RC2). In previous intensive monitoring campaigns of the River Swale, all the minor tributaries were sampled and analysed daily. These studies have shown that the minor tributaries only contributed 2.4 to 3% of the total water volume measured at Crakehill, and less than 2.3% of the total phosphorus load at Crakehill. For this reason, in the present study, the sampling frequency was reduced.

Chemical analysis

A 100 ml aliquot of each sample was filtered through a 0.45 µm cellulose nitrate membrane and analysed for soluble reactive phosphorus (SRP) using a spectrophotometric method modified from Murphy and Riley (1962) (Mackereth *et al.*, 1989). A sample of filtrate was retained for subsequent analysis of dissolved silicon and total dissolved phosphorus (TDP). The filtering and analysis of SRP was carried out within 24 h of the sampling, so as to minimize errors associated with sample instability (Haygarth *et al.*, 1995; House and Warwick, 1998a). Total dissolved phosphorus and total phosphorus (TP, comprising of TDP plus particulate-bound phosphorus) were determined by digesting filtered and unfiltered river water subsamples respectively, with acidic potassium persulphate in an autoclave at 121 °C, then reacting with acid ammonium molybdate reagent to produce a molybdenum–phosphorus complex. This intensely coloured compound was then quantified spectrophotometrically at 880 nm (Eisenreich *et al.*, 1975). The concentration of dissolved silicon (principally silicic acid) in the filtered samples was determined by reaction with acid ammonium molybdate, to form yellow molybdosilicic acids. These were then reduced using an acidified metol-sulphite

Table I. Details of sampling campaigns. Mean discharges were calculated from 15 min interval river gauging data

Sampling site		River Swale at Catterick Bridge	Bedale Beck at Leeming	River Wiske at Castle Farm	Cod Beck at Dalton	River Swale at Crakehill	Number of minor tributaries spot sampled
National grid reference		SE 225 994	SE 302 905	SE 375 844	SE 422 766	SE 426 734	
Catchment area above sampling site (km ²)		508	142	216	217	1457	
3–11 March 1998	Mean discharge (m ³ s ⁻¹)	44.2	3.0	23.37	2.87	80.0	
192 h duration	Sampling interval (h)	3	3	3	3	3	7
14–22 July 1998	Mean discharge (m ³ s ⁻¹)	6.3	0.83	0.42	0.68	11.2	
190 h duration	Sampling interval (h)	3	3	3	3	3	11
6–14 October 1998	Mean discharge (m ³ s ⁻¹)	8.5	0.61	0.31	0.38	10.9	
187 h duration	Sampling interval (h)	3	24	3	3	3	13
12–22 February 1999	Mean discharge (m ³ s ⁻¹)	9.3	1.29	0.68	1.28	13.5	
246 h duration	Sampling interval (h)	3	24	3	3	3	13

solution to form intensely coloured silicomolybdenum blues, which were quantified spectrophotometrically at 810 nm (Mullin and Riley, 1955; Mackereth *et al.*, 1989). Suspended solid concentrations were determined by filtering a known weight of previously unfiltered sample through a GF/F grade glass microfibre pad (0.7 µm) and then drying the filter and sediment for 24 h at 70 °C.

Residual mass-balance

The determinand concentrations of each sample and the corresponding river discharge data were used to calculate instantaneous loads, as follows:

$$L_i = C_i \times Q_i \quad (1)$$

where L_i , C_i and Q_i are the instantaneous load, concentration and river water discharge at the i th time period.

The total amount or flux (F) of a particular determinand transported past a gauging site between times t_i and t_{i+1} was calculated by:

$$F_i = \left(\frac{L_{i+1} + L_i}{2} \right) \times (t_{i+1} - t_i) \quad (2)$$

where F_i is the flux over the time interval.

The total cumulative flux for each sampling site was determined using:

$$M_j = \sum_{i=1}^j F_i \quad (3)$$

where M_j is the cumulative flux to time period j .

The cumulative fluxes at each of the sampling times were used to calculate a residual mass-balance for the river section.

The fluxes were first adjusted to take into account the transit time of the river between Catterick and the other sampling sites (i.e. it takes approximately 16 h for a flood pulse to travel down the River Swale from Catterick to Crakehill; therefore, 16 h was subtracted from the sampling times at Crakehill). The transit times for each campaign were determined by estimating the average lag times between all peaks in the hydrographs for each site. These estimated transit times over the four campaigns were as follows; Bedale Beck (3.5–6 h), River Wiske (7–12 h), Cod Beck (11.5–15 h) and Crakehill (14–17 h). The mass-balance for the river section is given by:

$$M_{j,\text{Crakehill}} = M_{j,\text{Catterick}} + \sum M_{j,\text{major}} + \sum M_{j,\text{minor}} + M_{j,\text{residual}} \quad (4)$$

$M_{j,\text{residual}}$ is the mass-balance residual at time period j , and is a measure of the internal riverine processes that are occurring within the section, and the summations are over all the major and minor tributaries in the study reach. In principle, if there were no internal processes acting upon a determinand, then the amount entering the monitored river section would equal the amount leaving at Crakehill, and the residual would therefore be zero. In practice, the residual also reflects errors in chemical analysis, river gauging measurements and transit time estimation, sampling errors, and errors in the estimation of the contribution of the minor tributaries. However, accepting these limitations, a negative mass-balance residual indicates storage of those compounds within the river system and a positive mass-balance residual indicates an export from the system.

At 6 h intervals throughout the campaign, the total amount of each determinand entering the monitored reach of the river was calculated by summing the cumulative fluxes, taking into account the lag times. The mass-balance residual, $M_{j,\text{residual}}$, was then calculated using Equation (4). This incremental approach allows subtle changes in the residual to be identified throughout the course of the field monitoring.

RESULTS AND DISCUSSION

The four monitoring campaigns covered a wide range of river flow conditions experienced in this part of the catchment, ranging from low-flow in July and October 1998, to the very high discharges of the March 1998 campaign. The mean water discharges for each campaign are given in Table I, and concentration data is shown in Table II.

Mass-balances

The percentage contributions of the upper River Swale and tributaries to the total fluxes at Crakehill are shown in Figure 2. The river discharge data show that the upper River Swale at Catterick makes by far the largest contribution to the total discharge of the lower River Swale, supplying between 55 and 75% of the discharge at Crakehill. The discharge residual, i.e. the total flux of water flowing through Crakehill minus the amount of water entering the River Swale *via* Catterick and the tributaries, was slightly positive for all monitoring periods, and probably reflects groundwater inputs to the River Swale. The residual varied between 1 and 7% of the total load for the spring and autumn sampling campaigns, suggesting that the gauging data used in this study must be very reliable. Discharge residuals of similar values have been obtained from previous studies of the River Swale (House and Warwick, 1998b). However, during the July 1998 monitoring

Table II. Concentration data from sampling campaigns

Campaign	Sampling site	TDP ($\mu\text{mol l}^{-1}$)			TP ($\mu\text{mol l}^{-1}$)			Si ($\mu\text{mol l}^{-1}$)			Suspended solids (mg l^{-1})		
		mean	min	max	mean	min	max	mean	min	max	mean	min	max
March 1998	Catterick	2.1	0.0	7.8	10.4	1.9	27.3	56.8	33.6	73.1	54.8	3.5	295
	Bedale Beck	8.6	1.1	29.6	14.3	2.8	68.7	101.7	83.0	109.7	55.2	0.0	505
	River Wiske	17.1	3.1	35.4	74.7	13.0	213.8	133.1	39.2	218.7	828.0	7.8	8333
	Cod Beck	9.6	2.8	23.3	27.5	4.3	84.4	124.6	80.8	350.9	129.2	1.6	836
	Crakehill	3.5	0.2	12.6	14.6	4.5	40.6	64.0	12.1	359.5	2262.2	9.6	52 012
July 1988	Catterick	1.8	0.5	6.8	5.6	2.9	11.4	52.7	17.1	100.3	21.0	2.3	169
	Bedale Beck	11.3	6.9	23.1	24.5	10.5	107.0	147.0	117.6	231.5	104.3	9.0	978
	River Wiske	43.4	33.3	56.6	49.9	35.5	77.2	47.2	25.6	90.6	4.5	0.3	50
	Cod Beck	16.9	8.6	28.4	20.5	12.7	34.9	154.0	118.3	186.7	12.7	2.4	49
	Crakehill	5.6	0.9	11.1	9.9	5.9	17.0	76.9	56.3	87.8	44.1	7.2	368
October 1988	Catterick	1.6	0.5	3.3	3.6	1.8	6.8	58.8	43.4	71.9	8.9	3.4	49
	Bedale Beck	13.6	9.6	17.7	17.2	11.6	22.6	139.9	126.3	145.7	5.0	1.5	7
	River Wiske	54.5	26.1	77.1	62.3	36.9	88.3	168.2	122.9	196.4	7.4	0.0	71
	Cod Beck	16.5	7.0	26.6	21.4	12.9	30.9	121.5	98.3	148.6	3.1	0.0	12
	Crakehill	3.7	0.9	6.8	10.9	4.9	24.5	78.0	54.4	91.6	76.2	7.4	371
February 1999	Catterick	1.8	0.3	5.8	3.2	1.2	6.7	72.4	44.1	104.8	4.2	0.0	38
	Bedale Beck	4.8	2.6	6.4	7.9	6.2	9.4	107.0	94.5	114.9	10.7	7.9	17
	River Wiske	23.6	15.9	34.3	30.5	21.3	50.5	132.9	111.6	158.5	19.6	11.8	62
	Cod Beck	5.8	0.8	10.0	9.2	5.4	15.9	116.1	84.7	126.8	8.6	0.4	48
	Crakehill	3.8	1.3	6.4	5.9	4.2	10.3	90.4	57.9	114.4	14.2	3.4	52

campaign, the discharge residual increased to 14% (Figure 2b). This increase was probably due to the larger relative contribution of groundwater to the total river discharge during periods of low-flow in the summer.

Figure 2 also highlights the relatively large generation of suspended solid material within the study reach, with the upper Swale and tributaries only contributing between 12 and 45% of the measured suspended load at Crakehill. The resulting large positive suspended solid residual is probably caused by a decrease in particle size of the rivers' load as it is transported downstream, due to attrition. As the particle size decreases, an increasing proportion of the total load will become entrained in the water column as suspended material. The large suspended sediment residuals may also be partly due to sampling errors, particularly during the March 1998 flood event. Water samples were taken from a fixed position above the river-bed, and therefore may tend to over-sample the suspended load due to depth gradients in suspended sediment concentration during spates. Another contributory factor to the positive sediment residual is the large inputs of fine alluvial material caused by channel incision, as well as riverbank and soil erosion. Previous studies have shown that the River Swale has the highest sediment yield of all the Humber rivers, with a mean annual export of $58.4 \text{ t km}^{-2} \text{ year}^{-1}$, due to its high proportion of cultivated land (Wass and Leeks, 1999). Bank erosion rates of 300 mm yr^{-1} are common within this study reach, and rates as high as 1.7 m yr^{-1} have been recorded (Lawler *et al.*, 1999). This erosion will be particularly active during periods of high discharge. This was demonstrated during the major storm of March 1998, when suspended solid concentrations at Crakehill reached 52 g l^{-1} .

The tributary mass-balance approach shown in Figure 2 clearly shows the major role that the River Wiske plays in delivering phosphorus and silicon to the main river. Despite only contributing between 4 and 7% of the total discharge at Crakehill under normal flow conditions (Figure 2b–d), the tributary delivered a third of the TDP and SRP to the river, and 20–25% of the TP. During periods of high discharge, the role of the River Wiske became even more significant (Figure 2a). The tributary's proportion of the total discharge increased to 30%, the TDP and SRP increased to 60%, and it contributed 50% of the TP to the main river.

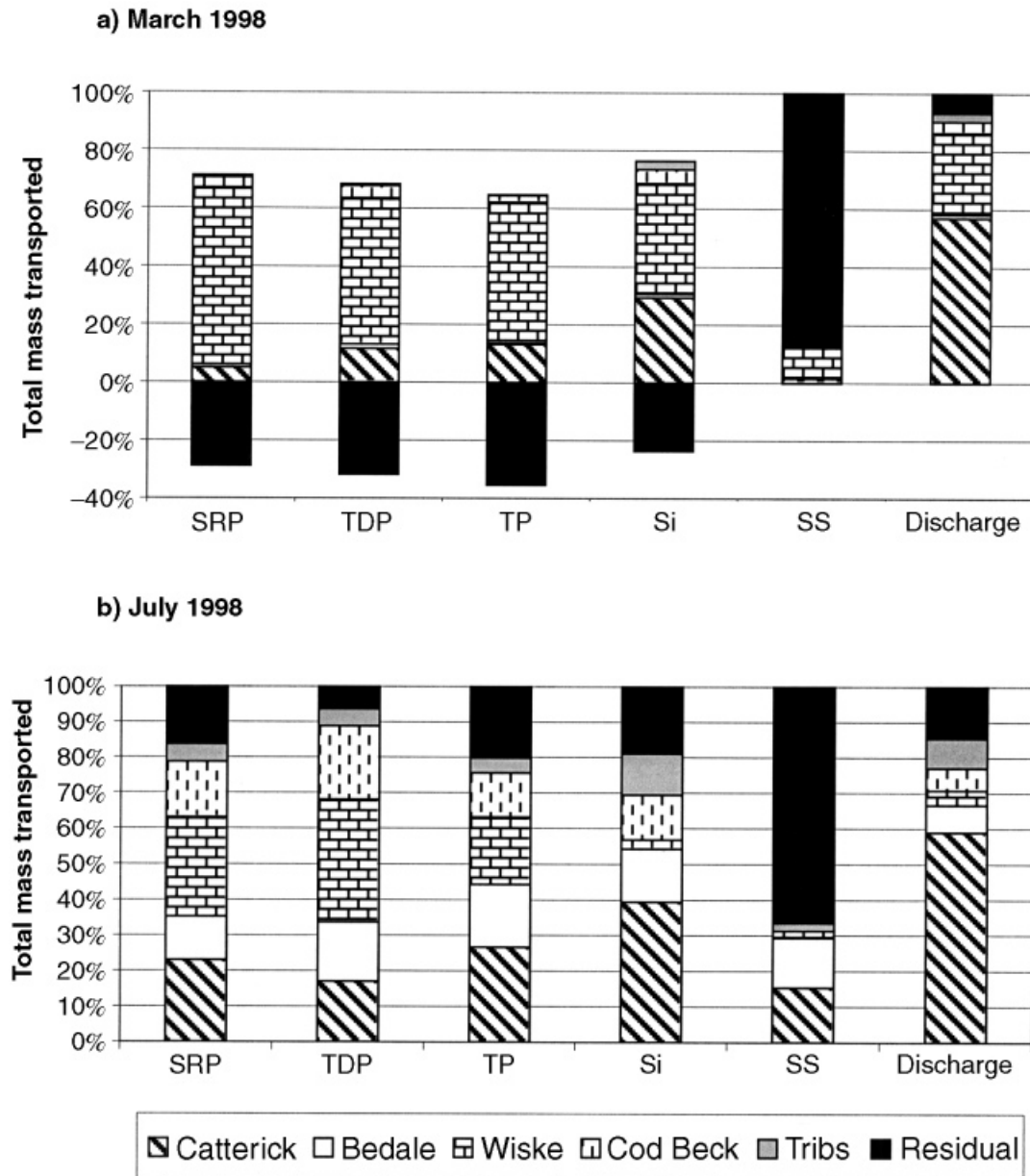


Figure 2. The contributions of the upper River Swale and tributaries to the total flux at Crakehill: (a) March 1998, (b) July 1998, (c) October 1998, (d) February 1999 campaigns. Key: SS = suspended solids

During this storm period, the River Wiske also supplied 40% of the dissolved silicon to the system. The major contribution of the River Wiske to the overall phosphorus budget of the River Swale catchment has also been observed in previous studies (House *et al.*, 1997).

During relatively stable periods of low to medium river discharge, there was a positive phosphorus residual (Figures 2b–d). This means that over the course of the campaigns, there was a mobilization of phosphorus within the river channel, and this accounted for up to 30% of the net-export of TP. The source of this

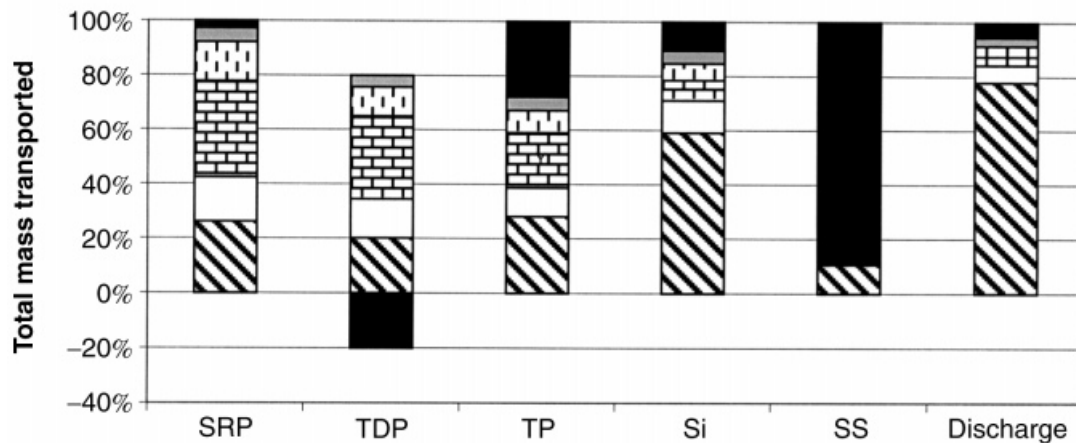
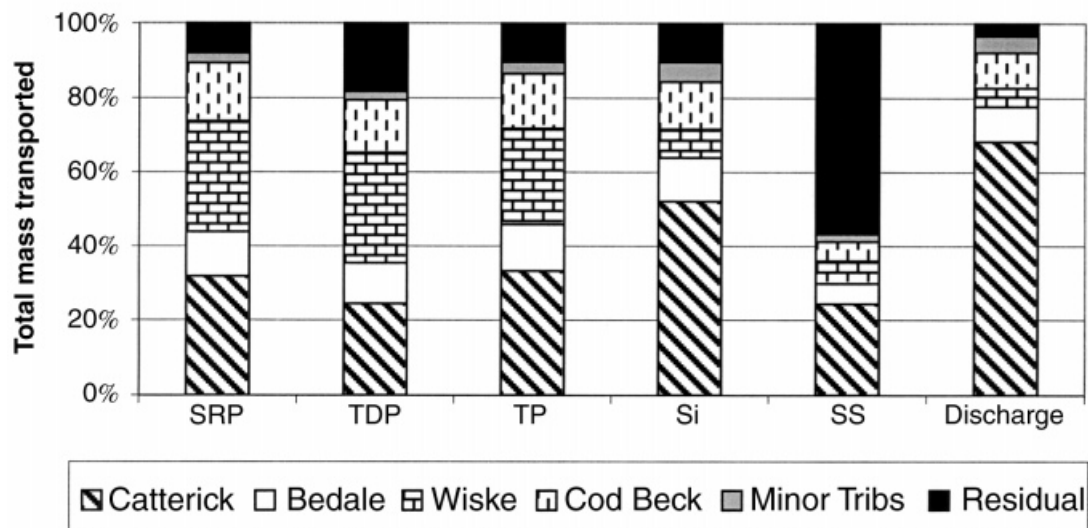
c) October 1998**d) February 1999**

Figure 2. (Continued)

phosphorus may be related to biotic factors, e.g. downstream drift of algae and plant material, diffuse phosphorus inputs, e.g. leaching of fertilizer from the floodplain, or the movement of P-rich sediment, e.g. mobilization of bed-sediments and phosphorus inputs due to riverbank erosion. As discussed below, these results are contrary to findings from previous studies of the River Swale, which have always shown negative phosphorus residuals under similar flow conditions (House and Warwick, 1998b). Hence, the antecedent conditions in the river channel may play a more important role in determining P-dynamics than previously thought.

Under the flood conditions of March 1998, there was a large negative residual for all phosphorus fractions. Approximately 30% of the phosphorus inputs to the river did not reach Crakehill, and were retained in the catchment. Most of this retention, *c.* 40%, was in the form of particulate P ($PP = TP - TDP$). Similar PP retention during periods of floodplain inundation has been observed in previous studies (Brunet and Astin, 1998).

The silicon mass-balance residuals showed a similar pattern to phosphorus over the four campaigns, with retention of silicon during the March 1998 flood event (Figure 2a), and a net release of silicon over the course of the other three monitoring periods (Figure 2b–d). This net-export of silicon will be caused by a combination of internal riverine processes and silicon input from groundwater. If we assume that the positive silicon residuals are entirely due to groundwater input, then the average concentration of silicon in the residual river water would need to be between 120 and 260 $\mu\text{mol l}^{-1}$. Groundwater silicon concentration data for the study area was not available, so the relative contribution of groundwater to the overall silicon budget could not be assessed.

Mass-balance development

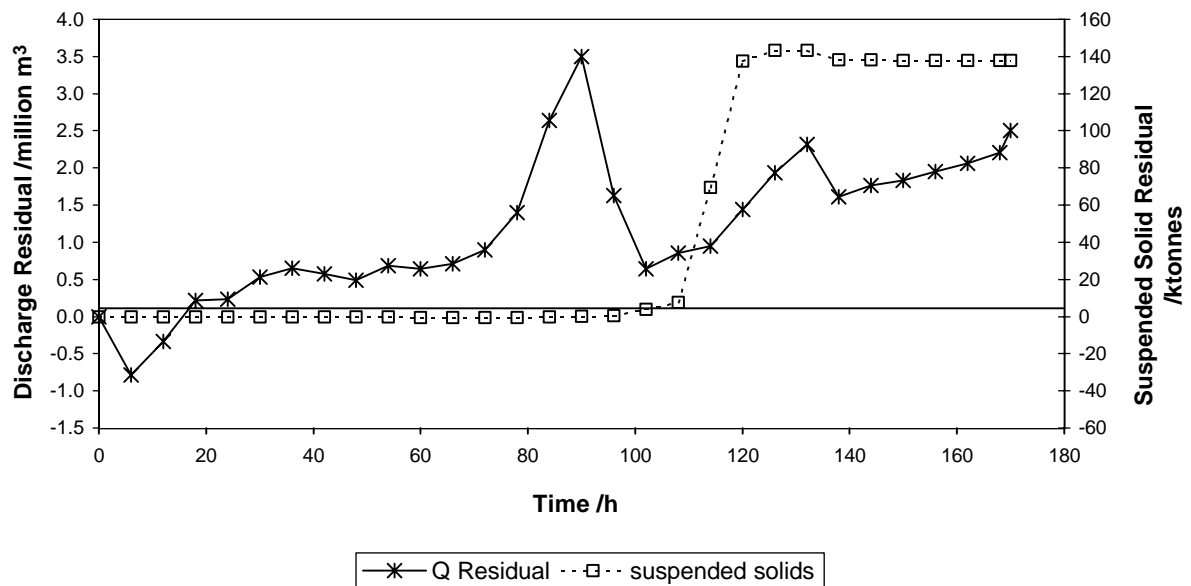
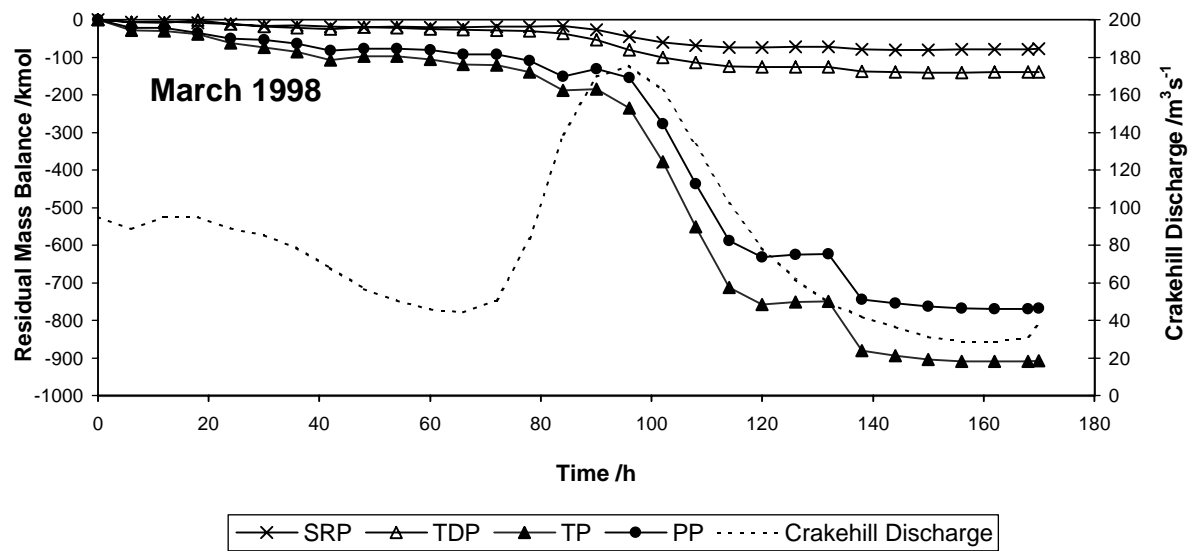
The incremental development of mass-balance residuals, calculated using Equation (4), throughout the course of each sampling campaign is shown in Figure 3. The discharge data from the Crakehill gauging station is also included in the figures.

March 1998 campaign

The monitoring period began near the end of a falling hydrograph, following a large storm. After 80 h of the campaign, there was a large and rapid rise in flow, caused by a combination of heavy rain and snowmelt. This resulted in major overbank flooding along the river valley from Crakehill to Morton-on-Swale (36 km upstream), and along the lower reaches of most tributaries. The flood event corresponded to the third largest discharge of the year.

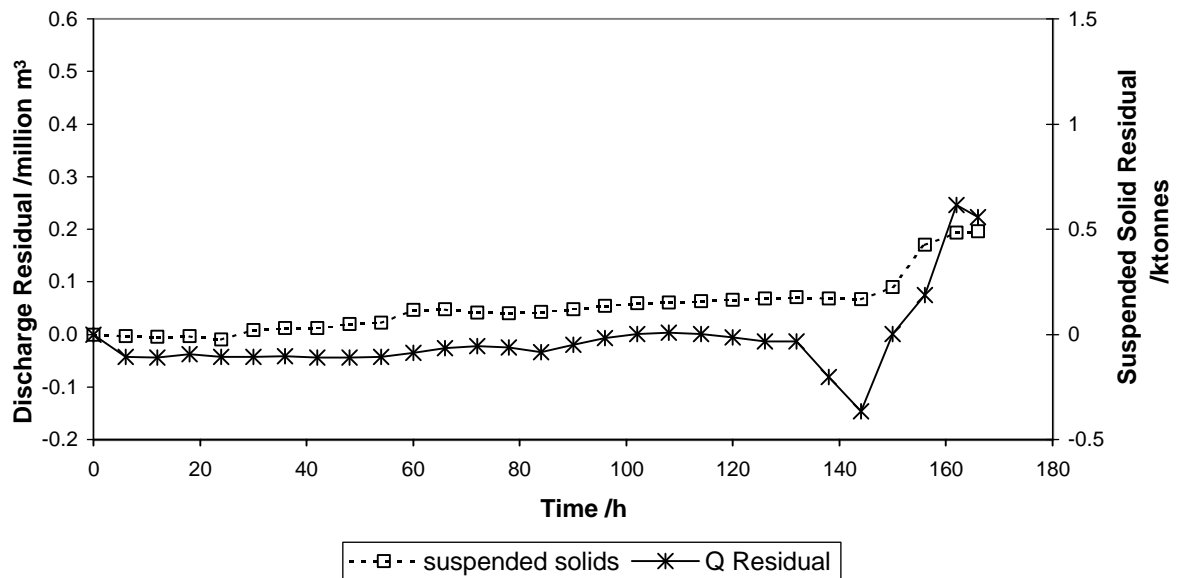
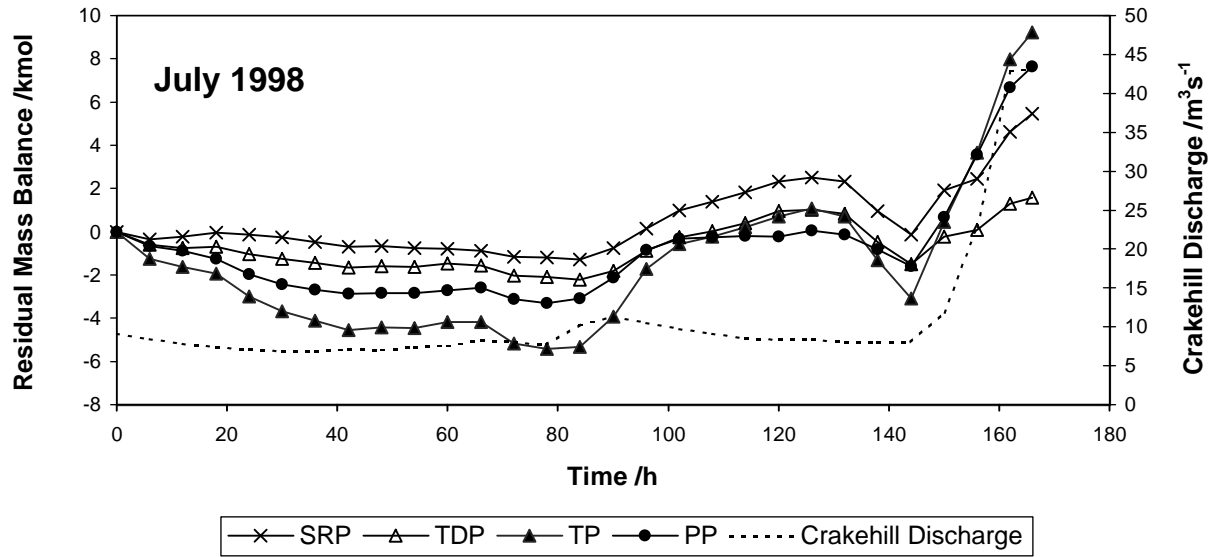
The March campaign produced TP fluxes that were 10 times higher than those observed in subsequent studies. There are a number of possible sources of this huge amount of phosphorus. Firstly, the large amount of rain and subsequent flooding during this period is expected to cause significant inwash of P from the floodplain (Johnson *et al.*, 1976). Secondly, the high discharge ($>150 \text{ m}^3\text{s}^{-1}$) of the River Swale and tributaries could mobilize and remove any remaining P-rich bed-sediment (Doriot *et al.*, 1989; Jordan-Meille *et al.*, 1998) and associated pore-water. This campaign also produced negative phosphorus residuals (Figure 3a), amounting to a retention of 900 kmol of TP in 170 h, i.e. 55% of the input. Over 80% of the phosphorus retained within the river system was in the form of particulate-bound P. During the initial falling hydrograph (from 0 to 80 h), both soluble and particulate phosphorus forms were being retained within the river, at a rate of 0.4 kmol h^{-1} , expressed as TP. This negative residual was attributed to PP being deposited within the River Swale channel as the discharge fell, and to the uptake of TDP and SRP by sediments. As the major flood passed through the river (75 to 130 h), the TP storage rate suddenly increased to *c.* 20 kmol h^{-1} , which is 64% of the flux at this time (Figure 3a). This was attributed to the large-scale movement of P-rich sediment from the river channel onto the floodplain during the flood event. This mass deposition and storage of sediment on the River Swale floodplain has been observed in previous studies, where it was estimated that 31% of the total suspended sediment delivered to the River Swale was lost in this way (Walling *et al.*, 1999).

The TDP and SRP residuals also became increasingly negative during the period of highest discharge. The flood resulted in very high concentrations of suspended solids (up to 52 g l^{-1} at Crakehill, much of which would originate from the erosion of low-P riverbank material and contribute to the gains in suspended solids shown in Figure 3a). Analysis of riverbank sediment taken from the River Swale at Maunby in 1996 (House and Warwick, 1999) has shown that the material has a very low equilibrium phosphorus concentration (EPC_0) of less than $0.1 \mu\text{mol dm}^{-3}$. Therefore, soluble reactive phosphorus entering the river would rapidly be sorbed onto suspended solids derived from bank material (House *et al.*, 1995). This transformation of soluble phosphorus to PP would result in an apparent storage of SRP and possibly TDP within the



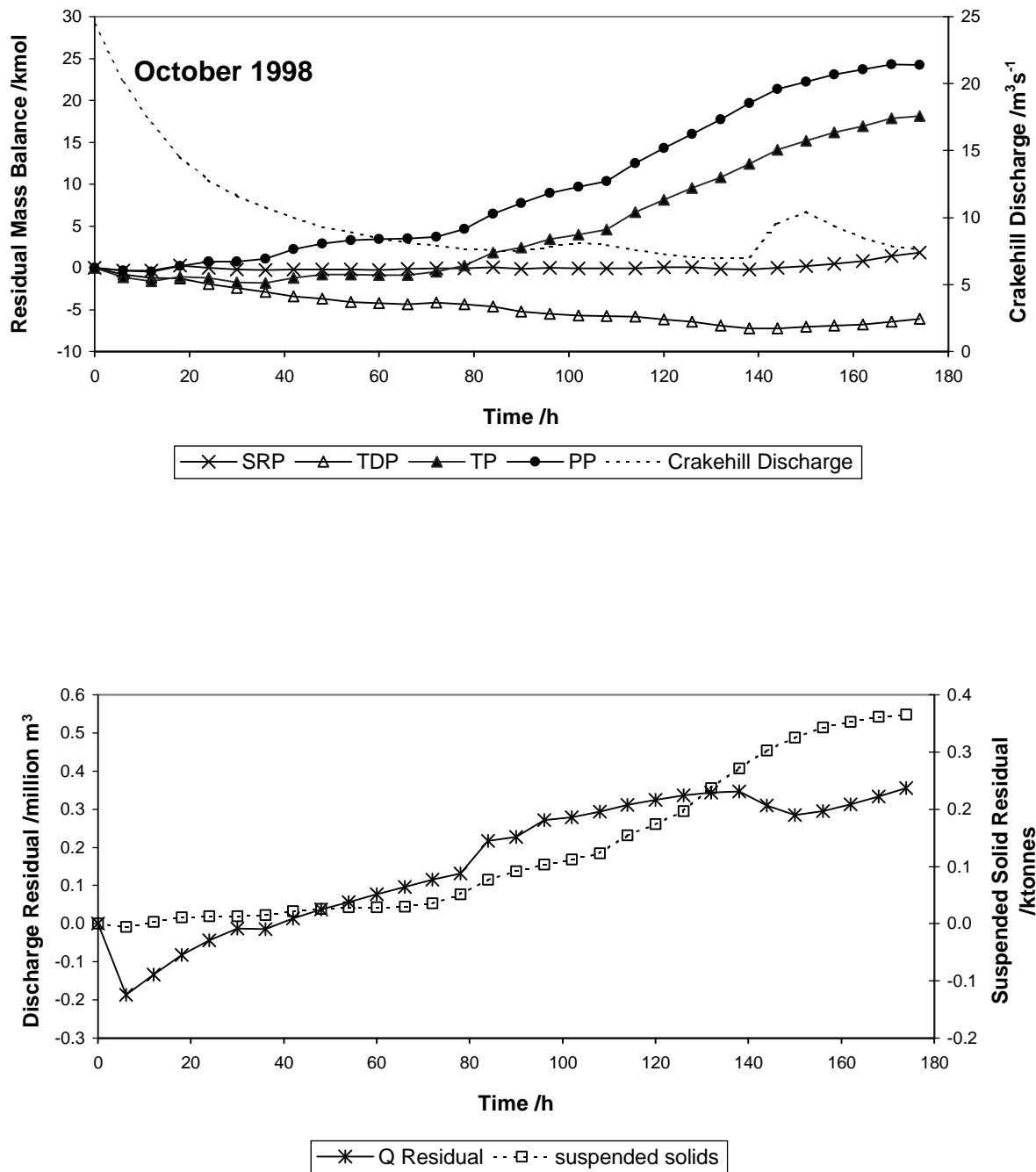
(a)

Figure 3. Mass-balance residuals: (a) March 1998, (b) July 1998, (c) October 1998, (d) February 1999 sampling campaign. Key: Q = discharge



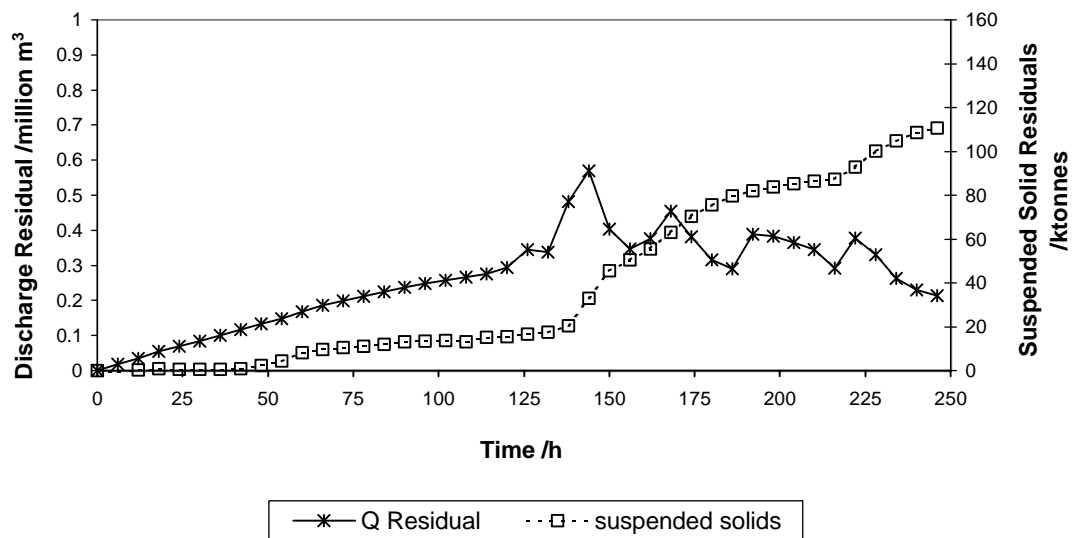
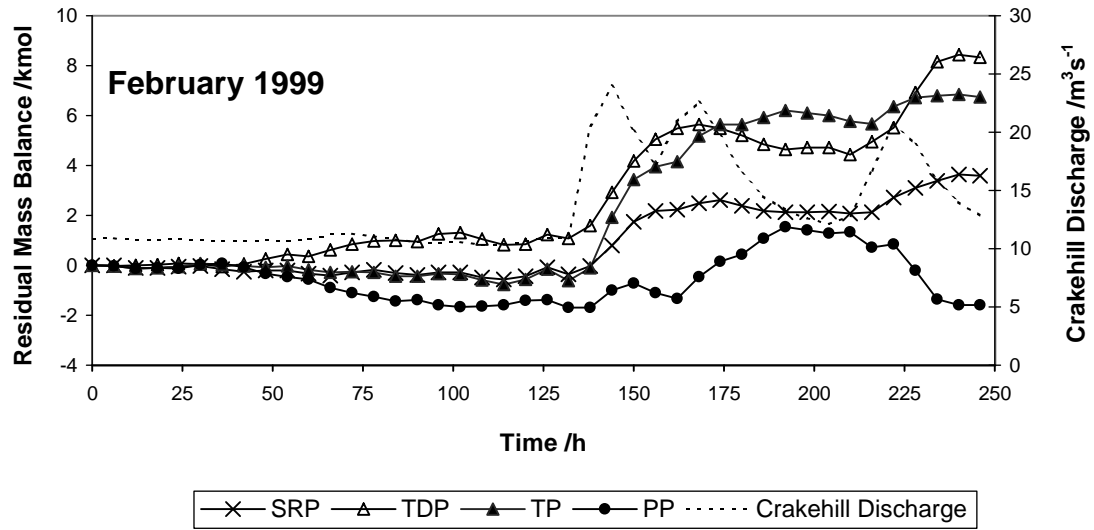
(b)

Figure 3. (Continued)



(c)

Figure 3. (Continued)



(d)

Figure 3. (Continued)

system. Another mechanism for the loss of soluble phosphorus is by infiltration of floodwaters into the floodplain, where much of the soluble P fraction will be retained within the alluvial deposits by a sorption process.

The mass-balance residual development for dissolved silicon is shown in Figure 4a. During the falling limb of the hydrograph (0 to 75 h), there is a small retention of silicon by the system, *c.* 2.5 kmol h⁻¹. This is unlikely to be caused by diatom assimilation this early in the spring and during storms, but may be a result of chemisorption of silicon to minerals in the bed-sediments (Beckwith and Reeve, 1963; Casey and Neal, 1983). Throughout the overbank flooding phase of the storm, the rate of silicon retention increased to 35.5 kmol h⁻¹. This sudden increase in retention rate corresponds to the onset of overbank flooding, and not the start of the rising limb of the hydrograph. This suggests that silicon must be being retained within the floodplain, rather than the river channel. One possible mechanism for this retention is by the chemisorption of silicon onto soil as it percolates through the floodplain deposits (Beckwith and Reeve, 1963). It has been suggested that these chemisorption reactions are controlled by the reaction of silicic acid with surface aluminium hydroxide groups of hydroxy-interlayered minerals (Sakagami *et al.*, 1993). As the flood passed through the system, the silicon retention rate rapidly reduced to *c.* 4.25 kmol h⁻¹, close to the value calculated before the flood. This pattern of retention is very similar to that of TP during this campaign. Similarities in the pattern of phosphorus and silicon dynamics have been observed in previous studies of spates in a small stream (Casey and Farr, 1982).

July 1998 campaign

This campaign was during a period of low river-flow (Table I). There had not been a storm pulse through the river system for 16 days prior to the start of the monitoring. A small storm pulse passed through the system between 80 and 100 h, followed by a much larger one after 145 h (Figure 3b).

During the initial period of stable low-flow (0 to 80 h), there was a gradual development of negative residuals for both soluble and particulate phosphorus (Figure 3b), similar to that observed in previous studies (House and Warwick, 1998b). The storage of PP in the system was most likely caused by the deposition of suspended sediments entering the river under these low-flow conditions. There were probably two internal riverine processes at work to cause the negative SRP and TDP residuals. Firstly, the soluble phosphorus fractions would gradually be sorbed onto the upper surface of the bed-sediments. Previous artificial channel experiments using River Swale bed-sediments have shown such uptake of soluble phosphorus when the SRP concentration is greater than the EPC₀ of the surface sediment (House and Warwick, 1999). Secondly, during the summer months, some of the bioavailable soluble P entering the river would be assimilated into biomass before reaching Crakehill, thereby producing a negative residual. SRP retention of river systems during low summer-flow conditions has been observed in previous studies (Johnson *et al.*, 1976; Aiba and Ohtake, 1977; Hill, 1981, 1982; Dorioz *et al.*, 1989; Brunet and Astin, 1998; House and Warwick, 1998b).

The dissolved silicon mass-balances (Figure 4b) also show retention during this period of stable low-flow, at a rate of 0.15 kmol h⁻¹. This retention is most likely caused by assimilation by benthic diatoms and possibly chemisorption to sediments. Artificial channel experiments using River Swale sediments in the absence of diatom biofilms have shown a net-release of silicon from the bed-sediments under similar steady low-flow conditions (House *et al.*, 2000), which suggests that in this case the dissolved silicon retention is due to biotic assimilation, rather than sediment uptake.

The small flood pulse at 80 h caused an immediate net-export of phosphorus (Figure 3b) and dissolved silicon (Figure 4b). The increase in discharge would mobilize the fine, P-rich upper bed-sediments, thereby increasing the PP loss. The increase in SRP and TDP residual is likely to have been caused by the inwash of soluble phosphorus that had accumulated on the floodplain, in the form of plant detrital material and animal faeces from bankside poaching by sheep and cattle over the previous 28-day dry spell, and also the diffuse losses of P in the form of fertilizer. The disturbance of the bed-sediments would also have accelerated

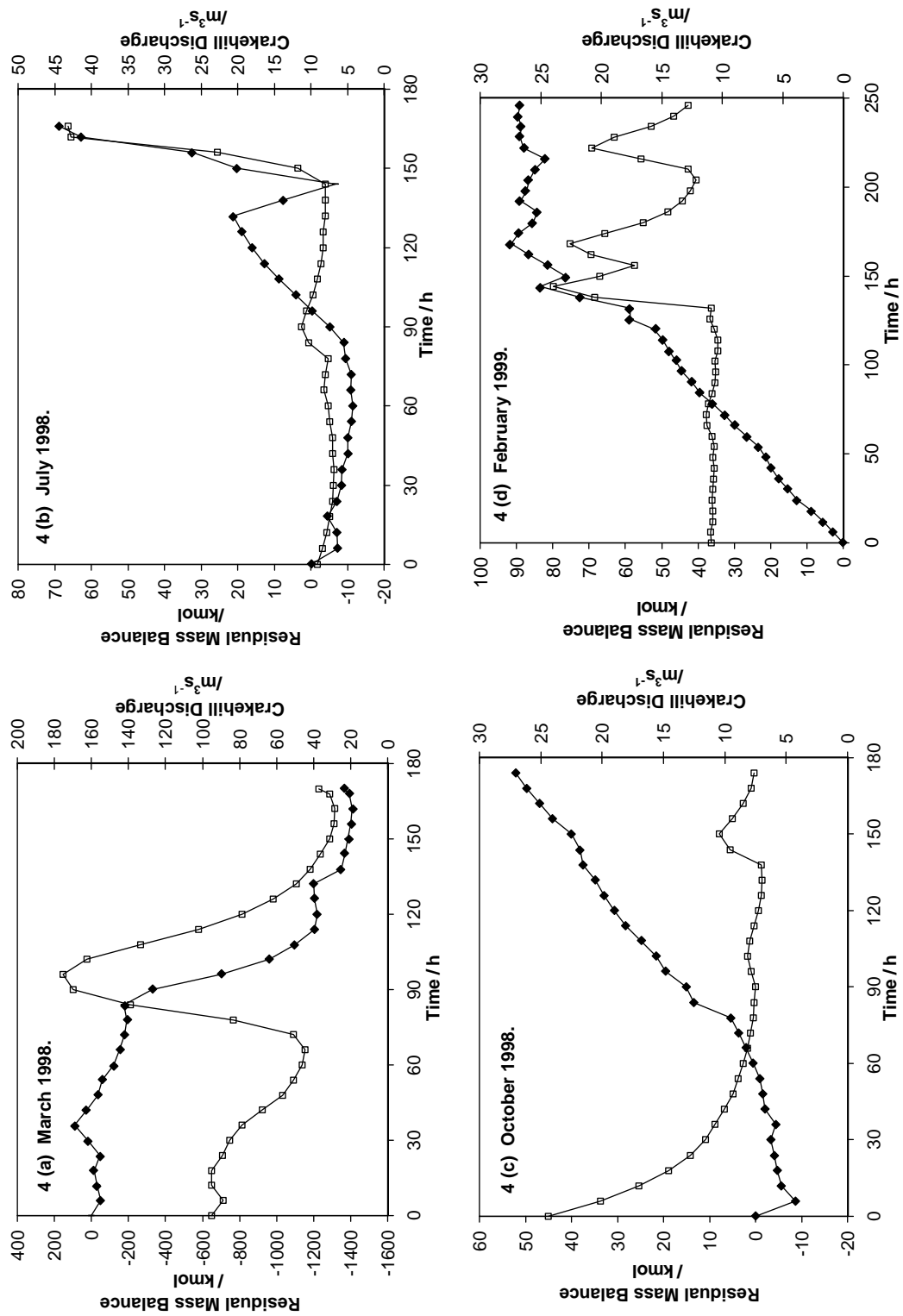


Figure 4. Dissolved silicon mass-balance residuals (\blacklozenge , kmol) and discharge at Crakehill (\square , m³ s⁻¹)

the release of Si-rich pore-waters into the water column, thereby surpassing biofilm uptake and producing a net-export from the river.

The rise in the hydrograph between 145 and 166 h resulted in a net-export of 12 kmol of TP, mainly in the form of PP and SRP. The increase in discharge again led to the mobilization of the bed-sediments, as shown by the increase in suspended solid positive residual (Figure 3b). These upper bed-sediments would have been sequestering dissolved P from the overlying water column since the last storm 28 days previously, and would therefore have a high phosphorus content. This is likely to be the source of the additional PP measured at Crakehill. Much of the gains in SRP and TDP were expected to arise from the input of phosphorus from the floodplain *via* surface runoff. However, another source of TDP and SRP generation within the river during this period could be the net release of P from the bed-sediments and P-rich suspended solids (Johnson *et al.*, 1976). The large input of more dilute waters from upstream and the tributaries into the River Swale, as well as rainfall interception by the river itself, would reduce the concentration of SRP and TDP by dilution. This would alter the phosphorus equilibrium between the bed-sediments and the water column, resulting in a reduction of the rate of adsorption, or even desorption of phosphorus. Previous studies have shown that River Swale bed-sediments have an EPC_0 of between 2 and $2.5 \mu\text{mol dm}^{-3}$ (House and Warwick, 1998a, 1999). The concentration of SRP at Catterick during this high-flow period dropped below the EPC_0 value to less than $1 \mu\text{mol dm}^{-3}$ (Table II), which is expected to lead to a net release of P from the bed-sediments into the water column.

The large increase in discharge between 145 and 166 h also caused a net loss of silicon from the system of 2.8 kmol h^{-1} , which is equivalent to a bed-sediment release rate of *c.* $61 \text{ mmol m}^{-2} \text{ day}^{-1}$, assuming a total bed area of $1.1 \times 10^6 \text{ m}^2$ (Figure 4b). This was again interpreted as being caused by the release of Si-rich pore-waters during the disturbance and mobilization of the bed-material.

October 1998 campaign

The first 90 h of the campaign was characterized by steadily falling river discharge. This was followed by two small peaks in the hydrograph at 90 and 140 h (Figure 3c).

Throughout the period there was a gradual net-export of PP and TP, and a retention of TDP by the catchment. This implies that, under these flow conditions, TDP was either being transformed to SRP and/or interacting with sediments in the system. Between 140 and 170 h, the SRP residual became positive, and the TDP residual remained constant. This was probably caused by the rainfall washing phosphorus from the floodplain into the main channel. This was the first significant rain in the lower part of the catchment for 8 days.

During the first part of the campaign, there was a gradual net-export of dissolved silicon throughout the falling limb of the hydrograph (Figure 4c). Between 80 and 170 h (a period of relatively stable low-flow), there was an increase in silicon net-export from the catchment, at a rate of 0.49 kmol h^{-1} . This is equivalent to an estimated silicon release rate from the River Swale bed-sediments of $10.7 \text{ mmol m}^{-2} \text{ day}^{-1}$. This was higher than had previously been measured during artificial channel studies using River Swale sediment of sand and gravel, where a maximum release rate of $4.9 \text{ mmol m}^{-2} \text{ day}^{-1}$ had been observed (House *et al.*, 2000). Higher rates may be expected from the finer, diatom frustule-containing sediments present within our study reach.

February 1999 campaign

There was no rain for the first five days of the campaign, so the first 130 h were characterized by a stable river discharge of $10 \text{ m}^3 \text{ s}^{-1}$ at Crakehill. During this time, there was a net-export of TDP, and a corresponding retention in PP within the system (Figure 3d). This suggests that suspended solids entering the river were being deposited onto the bed of the channel. This retention of PP within the system has been observed in previous periods of stable, low-flow, e.g. see the results for July in Figure 3b, 0–70 h. The net-export of TDP from the river may have been produced by the loss of detrital material, such as from the breakdown of plant and algal biomass, from within the system during autumn and winter. The TDP concentrations in the upper River Swale at Catterick showed a marked diurnal pattern, possibly due to the daily pattern of sewage discharge from STWs, with the highest concentrations observed at night, and lowest concentrations

during the early morning. These morning concentrations were often well below the expected EPC_0 value of the sediment, and thus lead to a net release of phosphorus from the sediments.

After 130 h, the river experienced three minor storm pulses of up to $25 \text{ m}^3 \text{ s}^{-1}$ at Crakehill (Figure 3d). This resulted in the total phosphorus residual becoming positive, showing a net-export of 7 kmol P from within the system. Most of the increase in TP was caused by the generation of TDP and SRP. There were two possible sources for this. Firstly, soluble P that had been accumulating on the floodplain during the previous dry spell would be washed into the river channel during the rainstorms as described previously for the July and October campaigns. Secondly, the input of rainwater into the river reduced the concentration of TDP and SRP from 2.5 down to $1 \text{ } \mu\text{mol dm}^{-3}$, which was well below the EPC_0 value for bed-sediment, resulting in a net release of soluble P to the overlying water. Further evidence for this dilution effect shifting the phosphorus equilibrium with the sediment is obtained by studying the changes in PP and suspended solid residuals. During the third storm peak (210 to 240 h), the PP residual becomes negative, but the suspended solid residual becomes increasingly positive (Figure 3d). This means that the increased flow resulted in a net-export of bed-sediments from the system, but this exported load had a reduced P concentration. This suggests that P was being released from the suspended solid load, because of the low phosphorus concentration in the surrounding water.

Dissolved silicon showed a similar pattern to TDP (Figure 4d), with a net loss from the system of 89 kmol over the course of the campaign. The loss during the period of stable low-flow amounted to a sediment release rate of $c. 9.7 \text{ mmol m}^{-2} \text{ day}^{-1}$ which is a similar flux to that measured in October in stable flow conditions. As the first flood pulse passed along the river system at 132 h, there was an immediate increase in the rate of silicon net-export, amounting to 2.1 kmol h^{-1} or $46 \text{ mmol m}^{-2} \text{ day}^{-1}$. A similar silicon release rate was observed during the rising limb of the July 1998 campaign. Some of this increase could also be attributed to the peak in discharge residual at this time. This could be caused by an error in the transit time estimate. During the storm pulses between 130 and 240 h, other mechanisms come into action that partly negate the net loss. Similar patterns of silicon dynamics have been observed in previous campaigns in this study, e.g. March 1998 during high-flows.

CONCLUSIONS

Observations of changes in phosphorus and silicon concentration and discharge in rivers alone give little insight into the internal processes that affect concentration occurring in the river channel. The use of incremental mass-balance residuals has proved an extremely useful experimental tool, enabling subtle changes in internal processes and rates of channel storage/remobilization to be identified.

Previous mass-balance studies on the River Swale have shown that a proportion of phosphorus entering the river was always being retained within the system over the duration of campaign, regardless of flow conditions and time of year (House and Warwick, 1998b). These observations now appear to be a result of the episodic nature of P remobilization and export (Johnson *et al.*, 1976; Meyer and Likens, 1979), exacerbated by the shorter duration of the monitoring campaigns (100 h). When the incremental mass-balance approach was applied to the data from these earlier sampling campaigns, it showed that all phosphorus residuals reacted in the same manner as observed in this study, with each campaign having periods of TP net-export during times of high river discharge.

Despite the complexity of the processes occurring within the River Swale catchment, the incremental mass-balance approach has shown that phosphorus residuals follow a relatively consistent pattern under various discharge conditions.

(a) During periods of stable low-flow

- There is a gradual retention of PP within the river, with rates of PP storage under steady base-flow conditions observed in this study varying between 15 and 40 mol h^{-1} , amounting to 16 to 43% of the total PP input.

- Negative TDP and SRP residuals develop, caused by chemical transformation and net uptake of soluble phosphorus by bed-sediments.
- The uptake rate of soluble P usually declines with time, as the phosphorus concentration of the surface sediment increases and approaches equilibrium with the overlying water.

(b) During high-flow conditions

- TP, TDP and SRP residuals become positive, indicating net-exports.
- There is a net loss of PP from the system, most likely caused by the mobilization and export of P-rich bed-material.
- There is a net-export of TDP and SRP, due to the release of P-rich bed-sediment pore-waters into the water column, release of P from suspended solids into the surrounding water, and the inwash of floodplain phosphorus by run-off.
- The size of the phosphorus export increases with increasing discharge, as higher flow rates will increase both the amount of sediment mobilization and the rate of phosphorus desorption, caused by the dilution effect.
- The time that has elapsed since the previous storm also has an affect on the size of the resulting positive P residual. A long dry spell results in large amounts of phosphorus being stored both within the bed-sediment and along the floodplain. Much of this stored P will be mobilized during the next spate, resulting in larger positive residuals.

(c) During overbank flooding

- A large proportion of phosphorus entering the River Swale is retained within the system.
- The majority of this phosphorus storage is in the form of PP, and is believed to be caused by the mass-deposition of suspended sediment onto the floodplain.
- The very high concentration of suspended solids during these flood periods (some of which will be P-deficient bank-eroded material) will sequester soluble reactive phosphorus from the water column, thereby resulting in large negative TDP and SRP residuals.
- The flood period during the March 1998 campaign resulted in storage rates of PP and TDP of 10.8 and 2 kmol h⁻¹, respectively, which amounts to 58 and 74% of the total input to the river.

Silicon mass-balance residuals are less easy to predict and interpret. However, correlations do exist between silicon residuals and river discharge.

- In periods of stable low-flow during autumn and winter, there is a net-export of silicon at a rate of *c.* 0.5 kmol h⁻¹ caused by the release of Si from sediment pore-waters into the water column. However, during the summer months, there is a slight storage of silicon within the system, probably caused by the bioassimilation of silicon by benthic diatoms.
- During the rising limb of the hydrograph, there is an increase in the net-export rate of silicon to a value of *c.* 0.25 kmol h⁻¹. This is equivalent to a sediment release rate of *c.* 50 to 60 mmol m⁻² day⁻¹, and is most probably caused by the release of Si-rich pore-waters into the water column as the bed-sediments are mobilized by the increased flow.
- The pattern of silicon residuals during falling limbs is inconsistent, with both losses and gains to the system being identified during these monitoring campaigns.
- During periods of overbank flooding, there is a large retention of Si within the system. This has been interpreted as being caused by the chemisorption of Si onto soils, as the floodwater percolates through the floodplain sediments.

The incremental mass-balance technique clearly highlights that, in a dynamic river such as the River Swale, the river channel should not be considered in isolation. The channel and floodplain must be treated as an integrated system, with nutrients being transferred between both units. The retention and subsequent remobilization of phosphorus and silicon within the river channel sediments is very dynamic, and occurs relatively frequently. The sorption of phosphorus by bed-sediments and assimilation by aquatic biota can retain phosphorus within the system for a matter of months. However, the only long-term sink for phosphorus is as particulate-bound P deposited onto the floodplain during overbank flow. Although these periods of overbank flooding are relatively infrequent, their impact on the phosphorus budget of the River Swale is significant. For the majority of the Holocene, the River Swale floodplain has been an aggrading system. The existing river terraces at Catterick have been dated as far back as the bronze age (Taylor and Macklin, 1997), which shows that overbank deposition of particulate bound phosphorus provides a mechanism for the long term loss of phosphorus from the aquatic system.

ACKNOWLEDGEMENTS

We thank MAFF for their financial support, David Lyndsay and Michael Stokes of the Environment Agency for supplying the river discharge data, and Dave Leach of the IFE for all his help during the monitoring campaigns.

REFERENCES

- Admiraal W, Mylius SD, Deruytervansteveninck ED, Tubbing DMJ. 1993. A model of phytoplankton production in the lower River Rhine verified by observed changes in silicate concentration. *Journal of Plankton Research* **15**: 659–682.
- Aiba S, Ohtake H. 1977. Simulation of $\text{PO}_4\text{-P}$ balance in a shallow and polluted river. *Water Research* **11**: 159–164.
- Beckwith RS, Reeve R. 1963. Studies on soluble silicon in soils. *Australian Journal of Soil Research* **1**: 157–168.
- Brown TH, Mahler RL. 1988. Relationships between soluble silica and plow pans in Palouse silt loamsoils. *Soil Science* **145**: 359–364.
- Brunet R-C, Astin KB. 1998. Variation in phosphorus flux during a hydrological season: The River Adour. *Water Research* **32**(3): 547–558.
- Casey H, Farr IS. 1982. The influence of within-stream disturbance on dissolved nutrient levels during spates. *Hydrobiologia* **92**: 447–462.
- Casey H, Neal C. 1983. Abiological controls on silica in chalk streams and groundwaters. In *Sediment and Water Interactions*, Sly G (ed.). Springer Verlag: New York; 311–342.
- Doriot JM, Pilleboue E, Ferhi A. 1989. Dynamique du phosphore dans les bassins versants: Importance deretention dans les sediments. *Water Research* **23**(2): 147–158.
- Eisenreich SJ, Bannerman RT, Armstrong DE. 1975. A simplified phosphorus analytical technique. *Environmental Letters* **9**(4): 5–53.
- Haygarth PM, Ashby CD, Jarvis SC. 1995. Short term changes in the molybdate reactive phosphorus of stored soil waters. *Journal of Environmental Quality* **24**(6): 1133–1140.
- Hetling LJ, Jaworski NA, Garretson DJ. 1999. Comparison of nutrient input loading and riverine export fluxes in large watersheds. *Water Science and Technology* **39**(12): 189–196.
- Hill AR. 1981. Stream phosphorus exports from watersheds with contrasting land uses in southern Ontario. *Water Resources Bulletin* **17**(4): 627–634.
- Hill AR. 1982. Phosphorus and major cation mass balances for two rivers during low summer flows. *Freshwater Biology* **12**: 293–304.
- House WA, Denison FH. 1998. Phosphorus dynamics in a lowland river. *Water Research* **32**(6): 1819–1830.
- House WA, Warwick MS. 1998a. Intensive measurements of nutrient dynamics in the River Swale. *Science of the Total Environment* **210/211**: 111–137.
- House WA, Warwick MS. 1998b. A mass-balance approach to quantifying the importance of in-stream processes during nutrient transport in a large river catchment. *Science of the Total Environment* **210/211**: 139–152.
- House WA, Warwick MS. 1999. Interactions of phosphorus with sediments in the River Swale, Yorkshire, UK. *Hydrological Process* **13**: 1103–1115.
- House WA, Denison FH, Armitage PD. 1995. Comparison of the uptake of inorganic phosphorus to a suspended and stream bed-sediment. *Water Research* **29**(3): 767–779.
- House WA, Leach D, Warwick MS, Whitton BA, Pattinson SN, Ryland G, Pinder A, Ingram J, Lishman JP, Smith SM, Rigg E, Denison FH. 1997. Nutrient transport in the Humber rivers. *Science of the Total Environment* **194/195**: 303–320.
- House WA, Denison FH, Warwick MS, Zhmud BV. 2000. Dissolution of silica and the development of concentration profiles in freshwater sediments. *Applied Geochemistry* **15**: 425–438.
- Jarvie HP, Neal C, Robson AJ. 1997. The geography of the Humber catchment. *Science of the Total Environment* **194/195**: 87–99.
- Jaworski NA, Groffman PM, Keller AA, Prager JC. 1992. A watershed nitrogen and phosphorus balance: The upper Potomac River basin. *Estuaries* **15**(1): 83–95.

- Johnson AH, Bouldin DR, Goyette EA, Hedges AM. 1976. Phosphorus loss by stream transport from a rural watershed: quantities, processes and sources. *Journal of Environmental Quality* **5**(2): 148–157.
- Jordan-Meille L, Dorioz J-M, Mathieu N. 1998. Approche experimentale par crue artificielle de la participation du reseau hydrographique a l'exportation de phosphore par un petit bassin versant rural. *Water Research* **32**(6): 1801–1810.
- Lawler DM, Grove JR, Couperthwaite JS, Leeks GJL. 1999. Downstream change in river bank erosion rates in the Swale–Ouse system, northern England. *Hydrological Processes* **13**: 977–992.
- Mackereth FJH, Heron J, Talling JF. 1989. *Water Analysis: Some Revised Methods For Limnologists*, Titus Wilson & Sons Ltd.: Kendal.
- Meyer JL, Likens GE. 1979. Transport and transformation of phosphorus in a forest stream ecosystem. *Ecology* **60**(6): 1255–1269.
- Mullin JB, Riley JP. 1955. The colorimetric determination of silicate with special reference to sea and natural waters. *Analytica Chimica Acta* **12**: 162–176.
- Murphy J, Riley JP. 1962. A modified single solution method for the determination of phosphorus in natural waters. *Analytica Chimica Acta* **27**: 31–36.
- Reynolds CS. 1986. Diatoms and the geochemical cycling of silicon. In *Biominalisation in Lower Plants and Animals*, Leadbeater BSC, Riding R (eds). Oxford University Press.
- Sakagami K, Nakahara O, Hamada R. 1993. Soluble silica in a tephra derived spodosol in the mountainous region of Chichibu, Japan. *Soil Science and Plant Nutrition (Tokyo)* **39**(1): 139–151.
- Taylor MP, Macklin MG. 1997. Holocene alluvial sedimentation and valley floor development: the River Swale, Catterick, North Yorkshire, UK. *Proceedings of the Yorkshire Geological Society* **51**(4): 317–327.
- Walling DE, Owens PN, Leeks GJL. 1999. Rates of contemporary overbank sedimentation and sediment storage on the floodplains of the main channel systems of the Yorkshire Ouse and River Tweed, UK. *Hydrological Processes* **13**: 993–1009.
- Wass PD, Leeks GJL. 1999. Suspended sediment fluxes in the Humber catchment. *Hydrological Processes* **13**: 935–953.
- Zhmud BV, House WA, Denison FH. 1997. Release kinetics and concentration profile of dissolved silicon in compacted sediments. *Journal of the Chemical Society, Faraday Transactions* **93**(19): 3473–3478.